REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-03-

0107

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPO
		15 Mar 2001 to 14 Mar 2002 FINAL

4. TITLE AND SUBTITLE
Fabrication and Characterization Facility for Molecule Elctronics

5. FUNDING NUMBERS
61103D
3484US

6. AUTHOR(S)
Professor Tao

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
FLORIDA INTERNATIONAL UNIVERSITY
SPONSORED RESEARCH OFFICE
UNIVERSITY PARK - PC 539
MIAMI FL 33199

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NE
4015 WILSON BLVD
SUITE 713
ARLINGTON VA 22203

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
F49620-01-1-0265

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION AVAILABILITY STATEMENT
APPROVED FOR PUBLIC RELEASE, DISTRIBUTION UNLIMITED

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

We have purchased and installed an ion beam coater that allows us to fabricate metal electrodes in conjunction with optical lithography techniques. The grain size of the metal electrodes evaporated by the ion beam coater is smaller than that prepared with the previously homemade thermal evaporator. Because the sample is allowed to rotate during evaporation, the thickness is also much more uniform. With these improvements our nanoelectrodes are significantly more reliable. We have also purchased a PC computer for data analysis and presentations.

For electronic measurements, we have acquired a probe station, semiconductor parametric analyzer, digital oscilloscope, spectrum analyzer and lock-in amplifier. The probe station is used to connect the molecular junctions on a chip to the measurement instruments. The semiconductor parametric analyzer provides accurate measurement of the electron transport current through single molecules at various bias voltages. The digital oscilloscope has a fast time response that is necessary for us to monitor transient events during the etching and molecular binding processes. The lock-in amplifier has been used to directly measure the differential conductance of the molecules. It also improves the signal to noise ratio of some of the measurements. The four units are described as follows.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Fabrication and Characterization Facility For Molecular Electronics

F49620-01-1-0265
Amount: **$153,501**

Final Report
4/1/01 -3/31/02

Nongjian Tao
Department of Physics, Florida International University, Miami, FL 33199
Present Address:
Department of Electrical Engineering, Arizona State University, Tempe, AZ85287
Tel: 480-965-4456, Fax: 480-965-8118, Email: nongjian.tao@asu.edu

OBJECTIVES

The objectives of this project are to seek a better understanding of electron transport in single molecules and to develop a molecular electronic device that can communicate with the outside world in a more practical way than the existing methods. In order to reach the objectives, we have proposed to acquire and set up a thin film fabrication system and electronic characterization equipment.

STATUS OF EFFORT

We have purchased and installed an ion beam coater that allows us to fabricate metal electrodes in conjunction with optical lithography techniques. The grain size of the metal electrodes evaporated by the ion beam coater is smaller than that prepared with the previously homemade thermal evaporator. Because the sample is allowed to rotate during evaporation, the thickness is also much more uniform. With these improvements, our nanoelectrodes are significantly more reliable. We have also purchased a PC computer for data analysis and presentations.

For electronic measurements, we have acquired a probe station, semiconductor parametric analyzer, digital oscilloscope, spectrum analyzer and lock-in amplifier. The probe station is used to connect the molecular junctions on a chip to the measurement instruments. The semiconductor parametric analyzer provides accurate measurement of the electron transport current through single molecules at various bias voltages. The digital oscilloscope has a fast time response that is necessary for us to monitor transient events during the etching and molecular binding processes. The lock-in amplifier has been used to directly measure the differential conductance of the molecules. It also improves the signal to noise ratio of some of the measurements. The four units are described as follows.

- Gatan Model 681 High Resolution Ion Beam Coater.

- M&M Manual Probe Station with micromanipulators.
- Agilent 4156B Semiconductor Parametric Analyzer.
- LC574AM digital oscilloscope with HDD PC card and 520 Mbyte Hard Drive.
- Stanford Research, Model 760 FFT spectrum analyzer.
- Stanford Research, Model SR850 digital lock-in amplifier.

ACCOMPLISHMENTS/NEW FINDINGS

The above equipment has dramatically enhanced our research ability in both fabrication of molecular junctions and electron transport measurements of the junctions. A few examples are given below.

Fabrication of nanoelectrodes with molecular scale gaps

We have developed a fast method with a built-in self-termination mechanism. The principle of this method is sketched in Fig. 1. It starts with a pair of electrodes separated with a relative large gap in water or in dilute electrolyte. When applying a bias voltage between the two electrodes, metal atoms on the anode are etched off, and the etched atoms dissolved into the electrolyte as metal ions deposited onto the cathode. As we have found experimentally, the dissolution (etching) takes place all over the anode surface, but the etched metal ions are guided by the electric field and deposited onto the sharpest point of the cathode. Consequently, the gap narrows and the two electrodes may eventually connect to each other. Since we are interested in forming a molecular scale gap between the electrodes, the etching and deposition processes must be terminated before final connection. While a feedback mechanism may be used for this purpose, we use a much simpler self-termination mechanism by connecting one electrode to an external resistor (R_{ext}).

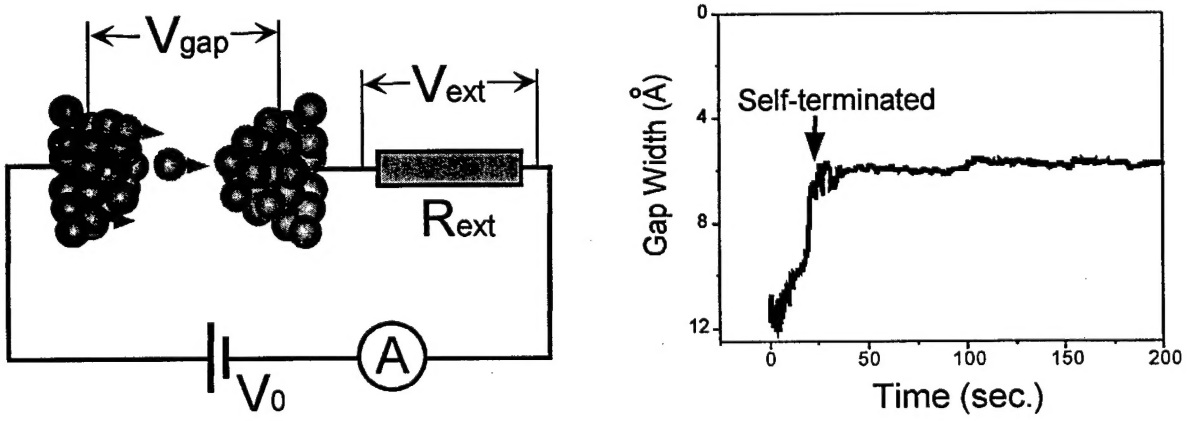

Fig. 1 Left: A self-terminated method for fabricating nanoelectrodes with a molecular scale separation. Right: A preliminary set of data shows a gap terminated at ~ 6 Å 20 seconds after applying a 1.2 V across the electrodes and external resistor. We note that at time=0 sec., the reading "12 Å", is due to a small but finite leakage current from ionic conduction. This error decreases exponentially as the gap width and becomes negligible when the gap is smaller than ~ 10 Å.

Connecting molecules to the nanoelectrodes

We have investigated electron transport through conducting polymer nanojunction formed between the nanoelectrodes. In sharp contrast to microelectrochemical transistor whose conductance varies smoothly between insulating and conducting states as a function of the electrochemical potential, the polymer nanojunction switches *abruptly* between the insulating and conducting (or off and on) states in a fashion similar to a digital switch (Fig. 2). The nanojunction can switch much faster and with less power than the bulk materials. We have also studied the I-V characteristics of the polyaniline nanowire. When the "gate" is kept near 0 V (vs. a Ag reference electrode), the I-V curve is linear, similar to that of a metallic wire. Lowering the "gate" below -0.2 V, however, the current vanishes at negative bias sweeps but it increases rapidly at positive bias sweeps. The rectifying characteristic is more pronounced when lowering the "gate" potential to -0.3 V. Our experiment shows that interesting new phenomena occur by reducing the size of the polymer junction.

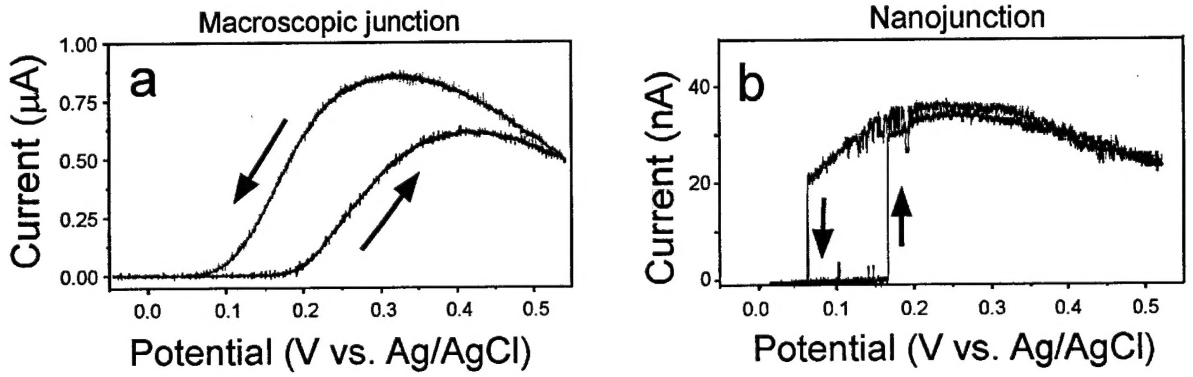

Fig. 2. A polyaniline nanojunction switch. Charge transport current vs. electrochemical potential for polyaniline nanojunctions with two Au nanoelectrodes separated with ~ 50 nm (a) and ~ 1 nm (b). The bias voltage between the nanoelectrodes in each case is 20 mV.

Another interesting observation of the polymer nanojunction is the discrete random fluctuation in the conductance between two or more levels. We have studied the switching by controlling the redox state of the polymer with the electrochemical potential of the nanoelectrodes. At negative potentials, the polymer is in the insulating reduced state and the conductance is always off. Increasing the potential, it switches abruptly between the on and off states. At high potentials, the polymer is in the oxidized state and the conductance stays predominantly in the on state. We attribute the telegraphic switching to a fluctuation in the redox states of a single polymer strand as electrons trap in or escape from the polymer. The on-off switching is likely related to the origin of the 1/f noise widely observed in polymer-based electronic and optoelectronic devices. In terms of chemical or biological sensor applications, if one wants to improve the sensitivity and response time by decreasing of the size of redox polymer sensing element (increasing the surface to volume), the telegraphic switching places a possible fundamental limit in the sensitivity of the sensor applications.

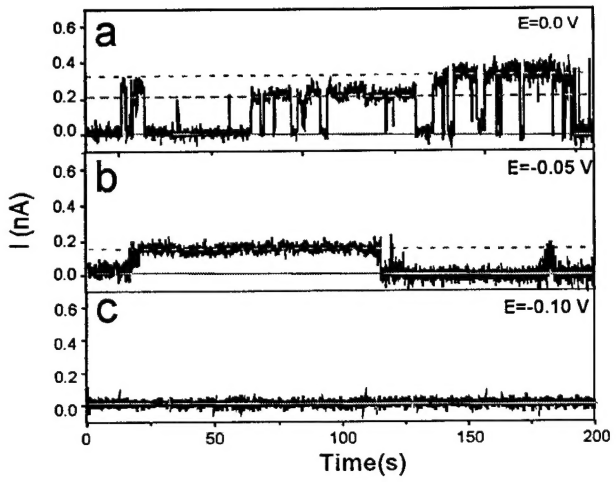

Figure 3. A multiple level conductance switching at various potentials. At high potentials, the conductance fluctuates between several levels. Decreasing the potential, a single two level on-off switch is left as the rest are permanently shut off. At more negative potentials, the conductance is zero.

Ionic adsorption onto metal quantum wires

Using the fabrication technique described above, we have fabricated metal quantum wires. We have determined the potential-induced modulation in conductance of Au quantum wires in electrolytes containing, F^-, Cl^-, Br^- and I^- (Fig. 4). These anions are known to adsorb onto Au electrodes with different strengths. At very negative potentials, no substantial anion adsorption takes place and the conductance modulation is similar for all the electrolytes. Increasing the potential, the conductance modulation increases as anions adsorb onto the wire. The dependence of the conductance change on the potential correlates well with the adsorption strengths of the anions, which is consistence with measurements performed on classical metal films. The significant increase in the conductance modulation upon anion adsorption is attributed to the scattering of the conduction electrons in the wire by the adsorbed anions. Because the wire is typical a few atoms long, enough to accommodate only a few ions, the sensitive dependence of the conductance on the adsorption suggests a method to detect a single or a few ions.

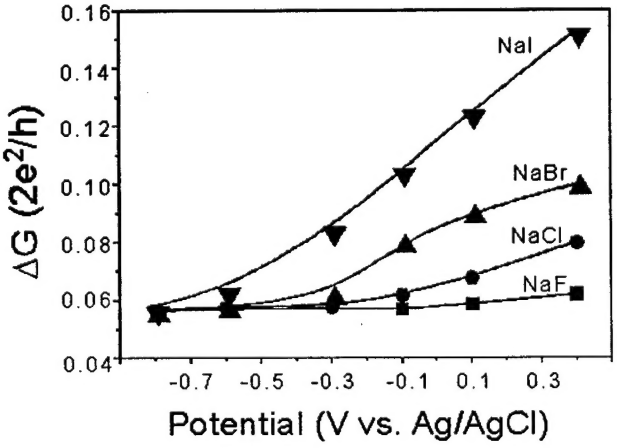

Fig. 4 Potential-induced conductance modulation vs. electrochemical potential for Au wires with conductance quantized near $1G_0$ in 0.5 M NaF, and in 0.5 M NaF containing 10 mM Cl^-, Br^- and I^-. The negative sign in front of ΔG means that an increase in the potential results in a decrease in the conductance. The amplitude of the applied electrochemical potential modulation is 0.05 V and the frequency is 1 kHz.

PERSONNEL BNEFITED FROM SUPPORTED

- Faculty
  N. Tao (Principal Investigator).

- Post-Docs
  C.Z. Li
  Katie He

- Graduate Students
  Alberto Bogozi
  Osvaldo Lam
  Chen Shu
  S. Hong

- Undergraduate Students
  Sergio Wong
  Joseph Bunch
  John Pean

PUBLICATIONS

Published:

1. H. X. He, J.S. Zhu, N.J. Tao, L.A. Nagahara, I. Amlani and R. Tsui "A Conducting Polymer Nanojunction Switch", J. Am. Chem. Soc., 123, 7730-7731, 2001.
2. S. Wang, S. Boussaad, and N. J. Tao, "Surface Plasmon Resonance - Enhanced Optical Absorption Spectroscopy for Studying Molecular Adsorbates", Rev. Sci. Instrum., 72, 3055-3060 (2001).
3. A. Bogozi, O. Lam, H. X. He, C.Z. Li, N.J. Tao, L.A. Nagahara, I. Amlani and R. Tsui "Molecular Adsorption onto Metallic Quantum Wires", J. Am. Chem. Soc., 123, 4585-4590(2001).
4. N.J. Tao, "Spectroscopic Applications of SPM in Electrochemistry" in "Encyclopedia of electrochemistry", Volume 2, edited by Bard and Stratmann, Wiely-VCH, in press, 2001.
5. S. Boussaad and N.J. Tao, "Atom-Size Contacts and Gaps Between Electrodes Fabricated with a Self-Terminated Electrochemical Method", Appl. Phys. Lett., 80, 2398-2400, 2002.
6. H.X. He, S. Boussaad, B. Xu, S. Bousssaad and N. J. Tao "Electrochemical Fabrication of Nanowires and Nanogaps", J. Electroanal. Chem., 522, 167-172, 2002.
7. H. X. He and N. J. Tao "Interaction of Molecules with Metallic Quantum Wires", Adv. Mat., 14, 161-164, 2002.
8. H. X. He, C. Shu, C. Z. Li and N. J. Tao, "Adsorbate Effect on the Mechanical Stability of Atomically Thin Metallic Wires", J. Electroanal. Chem., 522, 26-32, 2002.

INTERACTIONS/TRANSITIONS

Participation/Presentations At Meetings, Conferences, Seminars, Etc

INVITED TALKS:

1. Gordon Research Conference, Ventura Beach, CA, Jan. 21, 2002.
2. CSSER, Arizona State University, March 22, 2002.
3. Purdue University, seminar, "Connecting Single Molecules to Nanoelectrodes", May 9, 2002.
4. 200th Electrochemical Society Meetings, May 13, 2002.

NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

N.J. Tao, S. Boussaad and W.L. Huang, "High Resolution Surface Plasmon Spectroscopy", International Patent #WO0070328, 2001.

N.J. Tao and S. Boussaad "An Automated Method to Fabricate Arrays of Atomic-Scale Contacts and Molecular-Scale Gaps between Electrodes", U.S. Patent, 2001, Pending.

TECHNOLOGY TRANSFER

The quantum electronics lab of Motorola has been using the technique developed in this project to fabricated nanoelectrodes for molecular electronics applications. Semiconductor Research Corporation has provided a $35,000 to further develop the techniques to fabricated single molecular junctions.